Journal of Structural Chemistry, Vol. 46, No. 2, pp. 371-375, 2005
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CRYSTAL STRUCTURE OF BENZOIC ACID 4-NITROBENZYLIDENHYDRAZIDE

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UDC 548.736:547.574

The crystal structure of benzoic acid 4-nitrobenzylidenhydrazide has been determined. Crystal data: crystal system — monoclinic, $a = 7.101(9)$ Å, $b = 25.48(3)$ Å, $c = 7.730(11)$ Å; $\beta = 112.43(9)°$, space group $P2_1/n$, $Z = 4$, $R = 0.038$. The compound under investigation has a non-planar structure in general, and the substituents at azomethine N–C bond are in *E*-position. Root-mean-square planes of the six-memebered heterocycles make angles of 29.9° and 37.7° to fairly planar hydrazine fragment. In crystalline state the compound forms layers, the molecules within the layers being linked by C–H…O bonds. Neighboring layers are connected by hydrogen bonds between carbonyl oxygen atoms and amide hydrogens.

Keywords: benzoylhydrazone, C–H…O bonds, *E*-position of substituents, biological activity.

As it is well-known from literature [1], hydrazides of carbonic acid derivatives include a wide range of functional groups in their composition, and attract attention of researchers by a variety of structural peculiarities and the possible application as synthons for the broadest variety of heterocyclic compounds. Many of them (semi-, thiosemicarbazides, aminoguanidines, aroylhydrazides and their derivatives) possess the biological activity [2-4] and widely used in medical treatment of diseases induced by different pathogenic microorganisms. For these reasons, the search for optimum preparation conditions and structural investigation of novel representatives of these classes of chemical compounds are both of academic and practical interest.

The purpose of this work is the synthesis and ascertainment of structural peculiarities of benzoic acid 4-nitrobenzylidenhydrazide $4\text{-}NO_2\text{–}C_6H_4\text{–}CH\text{=}NNHC(O)C_6H_5$ (I).

Experimental. Benzoylhydrazone I was obtained as follows: a solution of 10 mmol of 4-nitrobenzaldehyde in 20 ml of ethanol was added under stirring to a warm solution (50-55°C, water bath) of 10 mmol of benzoic acid hydrazide in 50 ml of ethanol. A light-orange solution is formed, which yields a fine crystalline light-yellow precipitate on the slow evaporation during one day. The precipitate was collected on a frit, washed with ethanol and dried in air (yield 68%). Elemental composition of the material was established by chemical analysis.

Found, %: C 62.31; H 4.01; N 15.50. For $C_{14}H_{11}N_3O_3$ calculated, %: C 62.45; H 4.09; N 15.61.

IR spectroscopy data, cm^{-1}: $\nu_{as}(NH) = 3275$; $\nu_s(NH) = 3215$; $\nu(C{=}O) = 1645$; $\nu(C{=}N) = 1625$; $\nu_{as}(NO_2) = 1515$, 1345; $\delta(C\text{–}N) = 1195$, 1115; $\nu(N\text{–}N) = 975$; $\nu(C\text{–}N) = 970$, 930.

Azomethine I is readily soluble in dimethylformamide and dimethylsulfoxide, as well as in water or alcohols under heating. Single crystals suitable for X-ray diffraction study were obtained by the recrystallization from methanol.

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TABLE 1. Crystal Data, Experimental and Refinement Details for the Structure of I

Empirical formula	$C_{14}H_{11}N_3O_3$
Molecular weight	269,26
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell parameters, *a*, *b*, *c*, Å	7.101(9), 25.48(3), 7.730(11)
β, deg	112.43(9)
Volume, Å^3	1292(3)
Z	4
Density (calc)g/cm^3	1.384
Extinction coefficient, mm^{-1}	0.100
Crystal size, mm	0.4×0.3×0.3
θ range, deg	2.96-25.05
Measured reflections	2467
Independent reflections	2277 [R_{int} = 0.0632]
Data/parameters	2277/226
GOOF on F^2	0.962
Final *R*-factor [$I > 2\sigma(I)$]	$R1$ = 0.0382. $wR2$ = 0.0993
R-factor (overall)	$R1$ = 0.0657. $wR2$ = 0.1045
Largest peak and hole, eÅ^{-3}	0.170 and –0.194

TABLE 2. Positional (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2×10^3) for the Compound I

Atom	*x*	*y*	*z*	$U_{(eq)}$	Atom	*x*	*y*	*z*	$U_{(eq)}$
N(1)	2570(2)	2098(1)	5090(2)	45(1)	C(5)	2607(3)	1406(1)	2178(2)	48(1)
N(2)	2946(2)	2416(1)	6627(2)	45(1)	C(6)	2928(2)	1245(1)	3982(2)	41(1)
N(3)	2497(3)	125(1)	–161(2)	65(1)	C(7)	3149(3)	1624(1)	5473(2)	44(1)
O(1)	933(2)	3070(1)	4899(2)	53(1)	C(8)	2075(2)	2895(1)	6418(2)	40(1)
O(2)	2268(3)	274(1)	–1713(2)	103(1)	C(9)	2564(2)	3196(1)	8184(2)	40(1)
O(3)	2592(4)	–336(1)	260(3)	113(1)	C(10)	2790(3)	3737(1)	8142(3)	48(1)
C(1)	3117(3)	712(1)	4404(2)	51(1)	C(11)	3205(3)	4028(1)	9741(3)	64(1)
C(2)	2958(3)	345(1)	3048(2)	53(1)	C(12)	3347(3)	3792(1)	11373(3)	70(1)
C(3)	2654(3)	518(1)	1280(2)	47(1)	C(13)	3114(3)	3256(1)	11442(3)	66(1)
C(4)	2480(3)	1042(1)	817(2)	51(1)	C(14)	2727(3)	2955(1)	9844(2)	50(1)

X-ray diffraction experiment was performed using a Siemens P3/PC diffractometer (MoK_α-radiation, graphite monochromator, room temperature). Data collections were carried out in the θ/2θ-scanning mode. Absorption correction was not applied. The structure of I was solved by the direct methods using SHELX-86 program [5]. The refinement was made with SHELX-93 program package [6] in the anisotropic approximation for non-hydrogen atoms and in isotropic — for hydrogen atoms. Positions of the latter were found from differential Fourier syntheses. Basic crystallographic characteristics of the compound I and refinement parameters are listed in Table 1, independent atom coordinates are listed in Table 2, bond lengths and angles — in Table 3.

TABLE 3. Bond Lengths *d*, Å, and Angles ω, deg, in the Compound I

Bond	*d*	Bond	*d*
N(1)–C(7)	1.275(3)	C(4)–C(5)	1.378(3)
N(1)–N(2)	1.378(2)	C(5)–C(6)	1.387(3)
N(2)–C(8)	1.349(3)	C(6)–C(7)	1.465(3)
N(3)–O(2)	1.208(3)	C(8)–C(9)	1.486(3)
N(3)–O(3)	1.213(3)	C(9)–C(14)	1.387(3)
N(3)–C(3)	1.469(3)	C(9)–C(10)	1.388(3)
O(1)–C(8)	1.228(2)	C(10)–C(11)	1.374(3)
C(1)–C(2)	1.378(3)	C(11)–C(12)	1.366(3)
C(1)–C(6)	1.389(3)	C(12)–C(13)	1.380(4)
C(2)–C(3)	1.373(3)	C(13)–C(14)	1.389(3)
C(3)–C(4)	1.376(3)		
Angle	ω	Angle	ω
C(7)–N(1)–N(2)	114.70(16)	C(1)–C(6)–C(7)	119.13(17)
C(8)–N(2)–N(1)	119.97(15)	N(1)–C(7)–C(6)	120.88(17)
O(2)–N(3)–O(3)	122.84(17)	O(1)–C(8)–N(2)	123.16(14)
O(2)–N(3)–C(3)	118.8(2)	O(1)–C(8)–C(9)	121.93(17)
O(3)–N(3)–C(3)	118.38(18)	N(2)–C(8)–C(9)	114.90(15)
C(2)–C(1)–C(6)	120.84(18)	C(14)–C(9)–C(10)	119.38(16)
C(3)–C(2)–C(1)	118.35(19)	C(14)–C(9)–C(8)	121.95(18)
C(2)–C(3)–C(4)	122.36(15)	C(10)–C(9)–C(8)	118.63(15)
C(2)–C(3)–N(3)	118.26(19)	C(11)–C(10)–C(9)	120.16(19)
C(4)–C(3)–N(3)	119.38(17)	C(12)–C(11)–C(10)	120.5(2)
C(3)–C(4)–C(5)	118.74(18)	C(11)–C(12)–C(13)	120.28(19)
C(4)–C(5)–C(6)	120.41(18)	C(12)–C(13)–C(14)	119.9(2)
C(5)–C(6)–C(1)	119.28(15)	C(9)–C(14)–C(13)	119.8(2)
C(5)–C(6)–C(7)	121.55(17)		

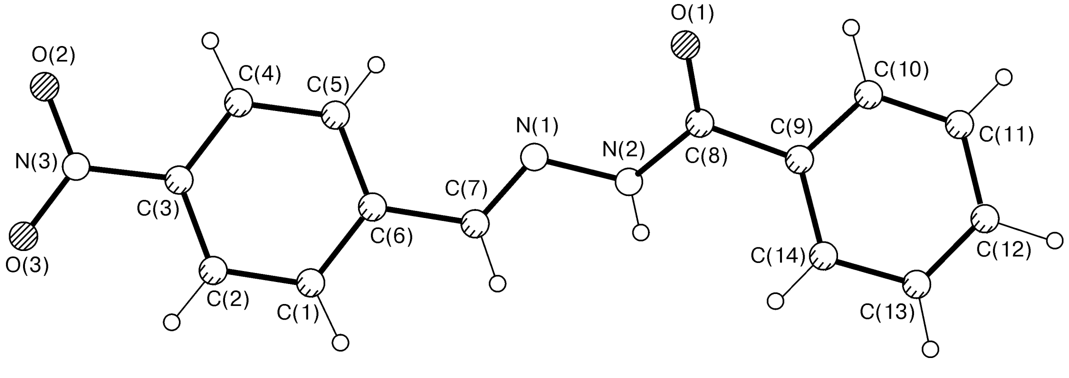

Fig. 1. Molecule of I.

Cambridge structural database (version 5.15, [7]) was employed in the analysis of geometrical parameters of I.

Discussion. In the compound I, as well as in benzaldehyde benzoylhydrazone (II) [8], salicylic aldehyde benzoylhydrazone (III) [9], *p*-(dimehtylamino)benzaldehyde benzoylhydrazone monohydrate (IV) [10], and *p*-methoxybenzaldehyde benzoylhydrazone monohydrate (V) [11], the substituents at azomethine bond N(1)–C(7) are in the *E*-position (Fig. 1), the molecule of I being non-planar. Root-mean-square planes of phenyl cycles C(1)÷C(6) (*A*) and C(9)÷C(14) (*B*)

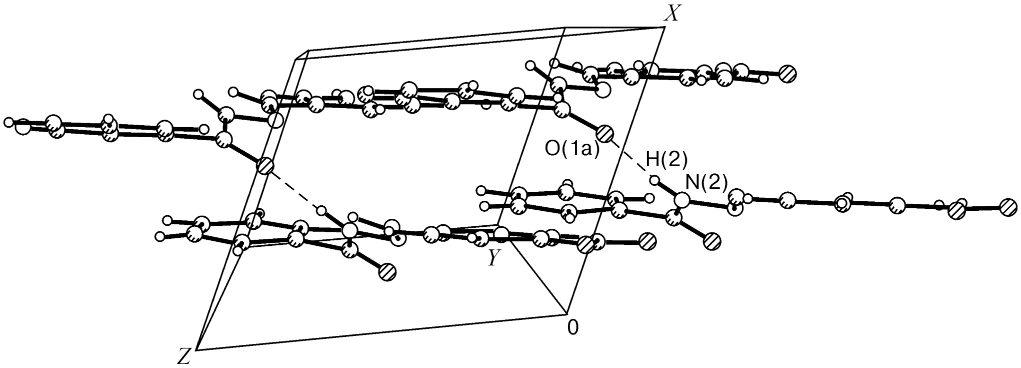

Fig. 2. Fragment of structure of I.

make angles of 29.9° and 37.7°, correspondingly, to hydrazine fragment N(1)N(2)C(8)O(1) which is planar. Corresponding angles in II are 19.1° and 24.1°, and in the molecules of III, IV, and V — 0 and 23.6°, 35.6° and 0, 43.1°, and 16.4°. At the same time, the angle between the planes *A* and *B* equals 10.2° in I. The nitrogroup attached to phenyl ring *A* is coplanar to it forming a joint π-system, the largest atomic deviation in 4-nitrobenzylidene fragment being less than 0.03 Å. The introduction of NO_2 group in the *para*-position elongates the bonds C(2)–C(3) and C(3)–C(4) in I, as compared to those in the compound II, which lacks the substituents in the relevant cycle. Thus, the mentioned distances are equal to 1.373(3) Å and 1.376(3) Å in I, while in II they have values 1.34 Å and 1.36 Å, respectively. A considerable difference amounting to 0.054 Å in C(8)–C(9) bond lengths is observed for the two compounds. The other bond distances in the molecule under investigation agree with the literature data. The atom C(7) of the molecule deviates from phenyl ring plane by 0.04 Å, and azomethine bond N(1)–C(7) also does not lie in this plane. The torsion angle C(5)C(6)C(7)N(1) is equal to 17.3°, while in the molecules of II and V this angle is close to 12°. Torsion angles C(6)C(7)N(1)N(2), C(7)N(1)N(2)C(8), N(1)N(2)C(8)C(9) and N(2)C(8)C(9)C(10) adopt the values of 177.4°, 167.6°, 178.8°, and 144.2°, correspondingly. In the molecule in question, hydrazine bond N–N is in the *gauche* conformation to C=O bond, the torsion angle N(1)N(2)C(8)O(1) is zero. The similar conformation of this fragment with analogous torsion angle values is realized in all the compounds mentioned above.

According to the criteria given in the paper [12], the molecules in the crystal of I are organized into layers by C–H…O bonds with the following parameters: C(10)…O(3)$^{/}$* 3.462(4) Å, H(10)…O(3)$^{/}$ 2.56(2) Å, angle C(10)H(10)O(3)$^{/}$ 156(2)°, C(12)…O(3)$^{//}$ 3.675(5) Å, H(12)…O(3)$^{//}$ 2.69(3) Å, angle C(12)H(12)O(3)$^{//}$ 155(2)°, C(1)…O(2)$^{///}$ 3.465(5) Å, H(1)…O(2)$^{///}$ 2.61(2) Å, angle C(1)H(1)O(2)$^{///}$ 152(1)°. The layers are linked by hydrogen bonds made by carbonyl oxygen atoms O(1) an amide hydrogen atoms at N(2): N(2)…O(1a) 2.887(4) Å, H(2)…O(1a) 2.02(2) Å, angle N(2)H(2)O(1a) 169(2)° (Fig. 2). Phenyl rings *A* and *B* of neighboring layers are arranged one over another, with the interplanar distances varying from 3.31 Å and 3.50 Å, which is typical of stacking interactions in the crystals [13]. The interaction between the layers in the crystal is of van der Waals nature.

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*Symmetry elements: ($^{/}$) $0.5-x$, $0.5+y$, $0.5-z$; ($^{//}$) $0.5-x$, $0.5+y$, $1.5-z$; ($^{///}$) x, y, $z+1$.

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